K·mol), suggestive of a transition state which has much less freedom than the adsorbed $-OCH_2CH_2O-$ species. No evidence of glycoaldehyde ($HOCH_2CHO$) production was found. The decomposition of ethylenedioxy is shown to proceed via an $O{=}CHCH_2O(a)$ intermediate by the appearance of new vibrational bands at 1730 and 2730 cm^{-1} assignable to aldehydic C=O and C—H stretches. The presence of coadsorbed oxygen atoms during the decomposition of $OCH_2CH_2O(a)$ results in very different chemistry and is the subject of a separate study.[18]

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation (NSFCBT 8701342) for this work. One of us (A.J.C.) wishes to express his appreciation to IBM for their support through a predoctoral fellowship.

Registry No. $(CH_2OH)_2$, 107-21-1; Ag(110), 7440-22-4; oxygen, 17778-80-2.

Photolysis of Amminepentacarbonylchromium in Hydrogen-Containing Matrices: Characterization of an H–H Stretching Vibration in Matrices

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Abstract: Irradiation of $Cr(CO)_5NH_3$ (I) in argon matrices doped with dihydrogen gives good yields of $Cr(CO)_5(H_2)$ (II). The high yields are obtained because the ammonia can be removed from I by photons the frequencies of which are not absorbed by II. The carbonyl bands of the infrared spectrum of II are perturbed by the presence of the nearby ammonia that had been ejected in the photodecomposition of I. Thus, the spectrum of II is somewhat altered from what is observed when II is formed from $Cr(CO)_6$ (III). With use of FTIR, adequate amounts of $Cr(CO)_5(H_2)$ have been prepared from both I and III so that most of the vibrational features between 4300 and 450 cm^{-1} have been observed, including the H–H stretch. The H–H stretching vibration gives rise to three absorptions at 3087, 3027, and 2997 cm^{-1}. The band at 3027 cm^{-1} exhibits a width at half height of 32 cm^{-1}, nearly twice the width of the other two bands. The relative prominence of the broad band at 3027 cm^{-1} correlates with the size of the host atom. In xenon and krypton matrices this band is most prominent, while in argon and, in particular, in argon doped with ammonia the two sharper bands are most prominent. Although the H–D stretch and the D–D stretch exhibit some unresolved splittings, the splittings are not nearly as large as that exhibited by dihydrogen, even allowing for the greater reduced masses of the heavier isotopomers. Mass-dependent splittings are also observed in the $Cr-H_2$ stretching vibration. The unusual bredth of the H–H stretching vibration at 3027 cm^{-1} is ascribed to the large torsional amplitude of diprotium. No theory explains the splittings that are observed in both the H–H and the $M-H_2$ stretching vibrations. Dynamic effects probably play a role in the splittings because the corresponding modes in the spectra of the heavier isotopomers are not split nearly as much.

It has been possible to synthesize a number of metal carbonyl dihydrogen complexes in inert gas matrices by irradiating stable 18-electron precursors with ultraviolet light.[1-4] Typically a carbonyl ligand is lost, and dihydrogen can compete with this carbonyl group for the vacated coordination site. The carbonyl group remains in the cage of any newly formed dihydrogen complex and can recoordinate if the dihydrogen vacates the coordination site. This reversal places a limit on the synthetic yield of the dihydrogen complex in a matrix because the ultraviolet photons that are used to remove the original carbon monoxide ligand are frequently capable of also causing the dihydrogen to be ejected. With prolonged irradiation, a photostationary state is established. Thus, in the matrix experiments that have been reported from this laboratory, the concentration of dihydrogen adducts has never been large enough for the observation of some key spectroscopic features, in particular the H–H stretching vibration.

A novel synthetic strategy was developed for dihydrogen complexes of the group 6 pentacarbonyls when it was recognized that the bonding between dihydrogen and the metal results in a significant d orbital splitting because of both σ and π interactions. The first observed optical transition for $Cr(CO)_5(H_2)$ occurs at 364 nm.[5] Reasoning that if an 18-electron precursor complex absorbed to the red of this transition, then it might be activated with light that the dihydrogen complex would not absorb. A whole class of colored $LM(CO)_5$ complexes exist in which L is a ligand that is capable of only σ bonding. Accordingly, $M(CO)_5NH_3$ for W and Cr were synthesized and matrix isolated in the presence of H_2. Irradiation with visible light produced large quantities of molecular hydrogen adducts. Here, we report the first observation of the H–H stretching vibration that has been observed at such low temperature and show evidence for the interaction of the ejected NH_3 with the carbonyl fragment. Subsequent to the initiation of this project, an FTIR was purchased and the enhanced signal-to-noise has made it possible to observe the H–H stretch of $Cr(CO)_5(H_2)$ formed from $Cr(CO)_6$. This has proven to be essential for the assignment of causes for the complexities that are herein reported.

Experimental Section

$Cr(CO)_5NH_3$ was prepared from $Cr(CO)_6$ by irradiating a dry THF solution with a medium pressure mercury lamp while bubbling NH_3 through the solution.[6] The crude product was concentrated and deposited onto an alumina column through which was passed hexane. This procedure stripped off the bulk of unreacted $Cr(CO)_6$. Subsequently, the

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$Cr(CO)_5NH_3$ was eluted from the column with THF. Usually, small amounts of $Cr(CO)_6$ contaminated the matrix. However, it was not affected when the matrices were irradiated with visible light sources. Matrices were formed by evaporating the $Cr(CO)_5NH_3$ from a glass container into a stream of matrix gas. The container was heated to temperatures ranging from room temperature to 45 °C. Temperatures were measured with use of a chromel–alumel thermocouple mounted on the container. When heated in vacuo $Cr(CO)_5NH_3$ undergoes some decomposition leading to the inclusion of small amounts of NH_3 and CO in the matrix. $W(CO)_5NH_3$ and $Mo(CO)_5NH_3$ were made in a similar fashion. The molybdenum complex did not survive heating under vacuum.

Argon and deuterium (Air Products) and hydrogen and xenon (Matheson) were over 99.99% pure and were used without further purification. Hydrogen (Air Products) of 99.9% purity was also used and occasionally was stored over CaH_2 to remove water impurities. Small amounts of water were usually present in matrices, rarely exceeding 0.1%. Also, some nitrogen and CO_2 have been evident. None of the features assigned to $Cr(CO)_5(H_2)$ correlated with the degree of purity of the matrix gas. HD was obtained from MCD Isotopes and was 98% pure. The Xe from unused Xe/H_2 mixtures was recovered for reuse by vacuum stripping of hydrogen at liquid nitrogen temperatures.

In several experiments the proportion of para hydrogen was altered from the amount characteristic of room temperature by storing the hydrogen at liquid nitrogen temperatures over Raney nickel for at least 12 h prior to using it to make up an argon/hydrogen mixture. The proportion of para hydrogen at room temperature is nearly 25%, whereas the proportion approaches 50% at 77 K.[7] The restoration of the room temperature distribution of nuclear spin states is slow in the glass bulb from which deposits were made. This was checked by measuring the relative intensities of the $S_0(0)$ and $S_0(1)$ rotational transitions of para and ortho hydrogen at 352 and 585 cm^{-1}, respectively.[8] Also, the ortho–para mixture was characterized by monitoring a pair of bands at 4140 and 4146 cm^{-1} which are associated with a perturbed H–H stretch of isolated hydrogen molecules. Similar bands are observed in Raman experiments.[9] This pair and the absorption at 585 cm^{-1} were routinely observed over the course of an experiment and no significant changes were observed over the course of an experiment.[7] Thus, the distributions of spin states of uncoordinated hydrogen are unperturbed over the course of the experiment.

Matrices were prepared with use of an Air Products Displex closed-cycle refrigerator; the configuration is similar to what has been previously found with use of a Fourier transform infrared spectrometer. A Beckman 4260 spectrophotometer was also used in early experiments and for the observation of the $S_0(0)$ transition of H_2. The spectrometer has been coupled to a Zenith Z-100 microcomputer for signal averaging. All frequencies that were measured by FTIR are reported without correction for the index of refraction of the atmosphere. The interferometer was operated without a cover on the sample chamber. Since the optics are sealed, the absorption from atmospheric gases were not objectionably strong. For observations in regions of atmospheric water absorptions, the difference spectrum was obtained by subtracting the background spectrum from the sample spectrum times a small factor that usually was within a few percent of unity. This procedure was not particularly successful in the region of 2350 cm^{-1} where CO_2 absorbs. Typically, the spectrometer was set for 1-cm^{-1} resolution and spectra were recorded from 4300 to 450 cm^{-1}. The spectra were transformed with use of Norton-Beer apodization. For observations that required high signal-to-noise, 100 scans were averaged. Xe matrices were so strongly scattering at 3000 cm^{-1} that the results of several experiments were added together in order to observe the H–H stretch.

Results

$Cr(CO)_5(H_2)$. When $Cr(CO)_5NH_3$ is irradiated with visible light in argon matrices containing hydrogen, it is efficiently converted into $Cr(CO)_5(H_2)$, a process that can be accurately summarized by the following equation.

$$\underset{\text{I}}{Cr(CO)_5NH_3} + H_2 \xrightarrow{\text{visible light}} \underset{\text{II}}{Cr(CO)_5(H_2)} + NH_3$$

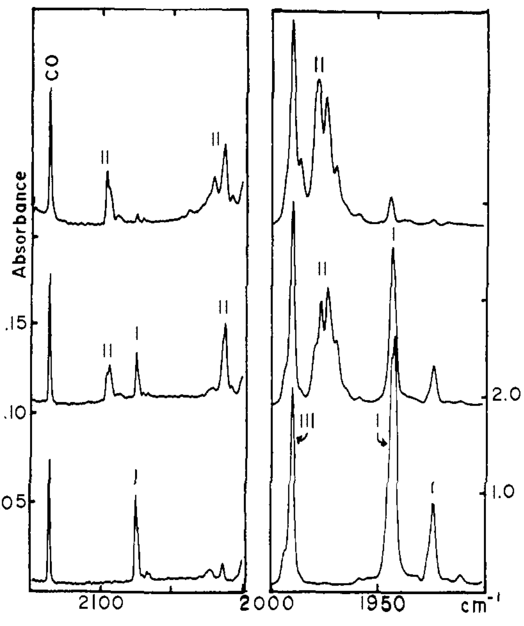

Figure 1. The bottom spectrum is the result of depositing $Cr(CO)_5NH_3$ for 30 min in an argon matrix doped with 20 mol % of hydrogen. The middle spectrum is of the same matrix after 3 min of irradiation with a 500-W projector lamp. The top spectrum shows the result of 310 min of irradiation. These latter two spectra show the conversion between differing forms of $Cr(CO)_5(H_2)$.

The process is most easily followed by observations of the carbonyl region of the infrared spectrum. $Cr(CO)_5NH_3$ is characterized by three principal absorptions ($2A_1 + E$). The bands are nearly symmetrical and less than 4 cm^{-1} in width at half-height, indicating that the molecule is well isolated and is not overly perturbed by the site. (See Figure 1.) Moreover, the spectrum shows that the 3-fold symmetry of the ammonia does not seriously perturb the 4-fold local symmetry of chromium. By contrast, the spectrum of the $Cr(CO)_5(H_2)$ that forms is substantially perturbed. A detailed description of those perturbations will follow below and is included in the supplemental material.

The photochemistry of $Cr(CO)_5NH_3$ (I) is dependent on the matrix identity, the presence or absence of hydrogen, and the spectrum of the incident radiation. Thus, in argon, an unfiltered, 500-W projector lamp causes very little loss of NH_3 even after prolonged irradiation, whereas the bands of I are rapidly attenutated in the presence of hydrogen as II is formed. By contrast, in pure xenon, irradiation of I with the projector lamp causes the formation of principally $Cr(CO)_5$ and NH_3, the process being nearly half-complete in 30 min. The loss of starting material is greatly accelerated when hydrogen is present. Then, bands due to II are observed to grow, in addition to bands due to $Cr(CO)_5$ and NH_3.

It appears therefore that visible light causes a simple substitution reaction, starting with the loss of ammonia. In argon, the ammonia efficiently recombines with $Cr(CO)_5$ except when a competing ligand such as dihydrogen is present. In xenon, the ammonia can successfully remain separate from $Cr(CO)_5$ even when a competing ligand is not present. The photochemistry of $LM(CO)_5$ has been extensively studied and, in particular, several matrix isolation studies have preceeded this report.[10] Irradiation into the longest wavelength portions of the absorption spectrum results in the loss of L when the LUMO is predominately composed of the d_{z^2} orbital. Radiation at higher frequency causes both CO and L loss. $Cr(CO)_5NH_3$ exhibits an absorption at 420 nm in argon matrices.[11] Although a detailed analysis of the frequency dependence of the

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[7] The room temperature distribution of ortho/para hydrogen is preserved in solid hydrogen for extended periods, changing only 2%/h. Silvera, I. F. *Rev. Mod. Phys.* **1980**, *52*, 393–451.

[8] The $\Delta J = 2$ transition is denoted by *S*, the vibrational transition is denoted by the subscript, and the *J*-state of origin is shown in parentheses. The pure rotational lines of hydrogen are seen because of couplings between phonon and translational modes. Warren, J. A.; Smith, G. R.; Guillory, W. A. *J. Chem. Phys.* **1980**, *72*, 4901–4908.

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[11] Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791–4800.

Table I. Comparison of Positions of Carbonyl Stretching and Deformation Bands for $Cr(CO)_5(H_2)$[a]

IIa	IIb	IIc	assignment
2095.3	2097.0	2097.0	A_1
		2035.0	?
2012.1	2019.5	2010.4[b]	B_1
	1987.0		?
1979.8	1978.3	1977.6	E + A_1
1976.8	1974.2	1973.3[c]	E + A_1
1973.5			E + A_1
1968.9			E + A_1
	670		E MCO deformation
	670 (663) [657][d]		A_1 MCO deformation

[a] IIa and IIb refer to two distinct forms of II that are observed when I is photolyzed in hydrogen-containing matrices. IIc refers to II that is formed from III. See supplementary material for a further discussion of the distinctions between the three forms. All peak positions are in cm^{-1}, obtained from FTIR spectra at nominal resolution of 1 cm^{-1}. The accuracy of the positions in many cases will be influenced by the presence of nearby absorptions. [b] Calculated wavenumber based on the force field reported in ref 5. [c] Frequency measured for D_2 isotopomer. Band is not resolved for H_2. [d] In situations in which there is a strong mass dependence, the position for the HD isotopmer will be in parentheses, that for the D_2 isotopomer will be in brackets.

photochemistry was not attempted, the use of a chlorine filter on the projector shows that λ can be longer than 400 nm and still result in ammonia loss. With λ = 254 nm, CO loss processes also occur as evidenced by the growth of the band due to free CO. Also, new bands appear in the carbonyl region that are easily photobleached with the projector lamp. Although these new species are undoubtedly produced by CO loss, their identities were not determined.

With use of the unfiltered projector lamp, it appears that Xe and Ar matrices exhibit different cage effects, but, in reality, the differences are probably due to the influence of argon and xenon on the absorption spectrum of $Cr(CO)_5$. The projector lamp is a more intense source at the position of λ_{max} of $Cr(CO)_5$ in Ar (533 nm) than at 492 nm, the position of $Cr(CO)_5$ absorption in Xe.[11] If the quantum yields for $Cr(CO)_5$ reaction with either CO or H_2 were the same in both matrices, $Cr(CO)_5$ would still appear to be more reactive in argon than in xenon because of the greater light intensity at 533 nm. To test this view, an argon matrix of $Cr(CO)_5$ was irradiated with the projector lamp through cobalt glass which absorbs light in the region of 533 nm. Then, good yields of $Cr(CO)_5$ were obtained, whereas unfiltered light would produce virtually no $Cr(CO)_5$ over the same time interval.[12] Once the dihydrogen occupies the coordination site, the ejected ammonia remains in the immediate vicinity of II because of its mass and the rigidity of the matrix. In this position, it can interact with II and hence perturb the spectrum of the products.

The presence of ammonia in the vicinity of II causes the spectrum in the carbonyl region to differ from that of II which is formed from $Cr(CO)_6$.[1,5,13] Just as one expects three principal carbonyl bands for I, three carbonyl bands are expected for II, two of which happen to be nearly accidentally degenerate.[5] The spectrum of II formed from I is much more complex as can be seen in Figure 1. The positions of bands are tabulated in Table I. For example, the totally symmetric A_1 vibration is split into two components, the formally forbidden transition of B_1 symmetry gains considerable intensity, and the band of E symmetry is split into several absorptions. Infrared bands are often split by perturbations caused by the trapping site in matrices.[14] In this instance, the perturbation is caused by the presence of the ammonia molecule which had previously occupied a coordination site on chromium; similar perturbations are not observed for II formed from $Cr(CO)_6$. At least two types of trapping sites were characterized. The nature of interactions of ammonia with II was studied in detail and described in the supplementary material. In summary, the perturbations on the carbonyl bands caused by ammonia still depend on the mass number and concentration of the hydrogen. Also, the symmetric deformation mode of ammonia shows a remarkable shift from its ordinary position in hydrogen-containing matrices. It is important to point out that the complexity in the H-H stretching region that will be described

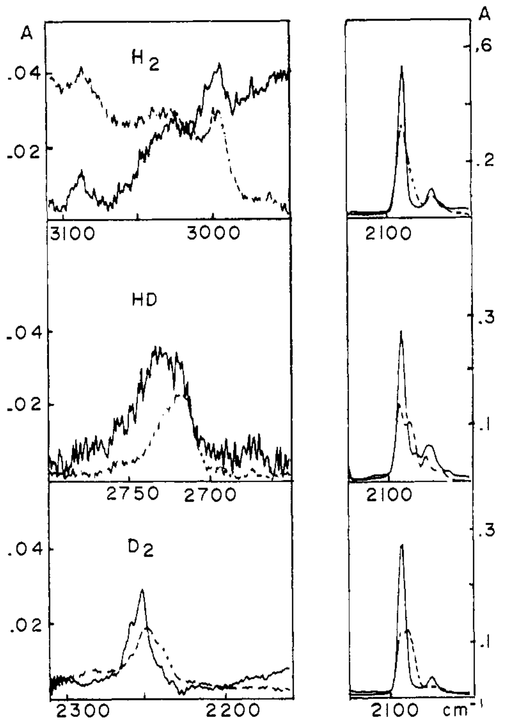

Figure 2. The H-H stretching vibration is shown as a function of atomic mass. The dashed lines are from spectra of $Cr(CO)_5(H_2)$ that was formed from $Cr(CO)_5NH_3$. The solid lines are from spectra of $Cr(CO)_5(H_2)$ that was formed from $Cr(CO)_6$. In order to facilitate the comparisons, the intensity scales were adjusted so that the area under the totally symmetric breathing mode at 2095–2097 cm^{-1} was the same in either sample for a given isotopomer. The procedure is flawed for the spectra involving HD. Small amounts of $Cr(CO)_5$ were formed because 254-nm radiation was used, in part, to form $Cr(CO)_5(HD)$. This has resulted in additional intensity at 2090 cm^{-1}, making the comparison of areas more difficult. Bands due to CH_4 and combination bands of $Cr(CO)_6$ are subtracted from all the spectra.

Table II. Summary of Hydrogen-Containing Vibrational Coordinates for $XYCr(CO)_5$[a]

	source		
	$Cr(CO)_5NH_3$	$Cr(CO)_6$ matrix	$Cr(CO)_6$ liq Xe[b]
XY = HH	3087 (15)[c]	3088	
	3027 (32)	3027	3030 (38)
	2997 (13)	2997	
	1380 (32)	1380	1379
	878.2	obscurred	not reported
	868.7	866.8	not reported
XY = HD	2727 sh	2724 (35)	2725 (30)
	2714 (22 collectively)		
	743.5	742	not reported
	737.6	735	not reported
XY = DD	2248 (19 collectively)	2253 (8)	2242 (16)
	2241 sh		
	680.1 unsym	679 unsym	

[a] All peak positions are in cm^{-1}, obtained from FTIR spectra at nominal resolution of 1 cm^{-1}. The accuracy of the positions in many cases will be influenced by the presence of nearby absorptions. [b] Reference 9. [c] Numbers in parentheses are widths at half-height.

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(12) Dramatically different quantum yields were observed for the reaction of $Mo(CO)_5$ + CO in argon and methane matrices. If one accepts that specific host-guest interactions dominate in methane, the quantum yield difference between argon and xenon probably will not be as large as that between argon and methane. Poliakoff, M. *J. Chem. Soc., Faraday Trans. II* **1977**, *73*, 569–573.

(13) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645–3651.

(14) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262–270.

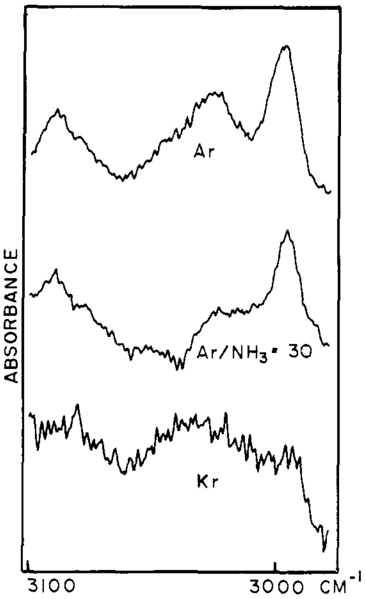

Figure 3. A comparison of the H–H stretching region of $Cr(CO)_5(H_2)$ in three different matrices doped with 20 mol % of hydrogen. They show how the profile of the bands in the region from 2990 to 3100 cm^{-1} changes as a function of the host matrix. The spectra were created by taking differences of spectra before and after irradiation so that a band due to CH_4 is not observed.

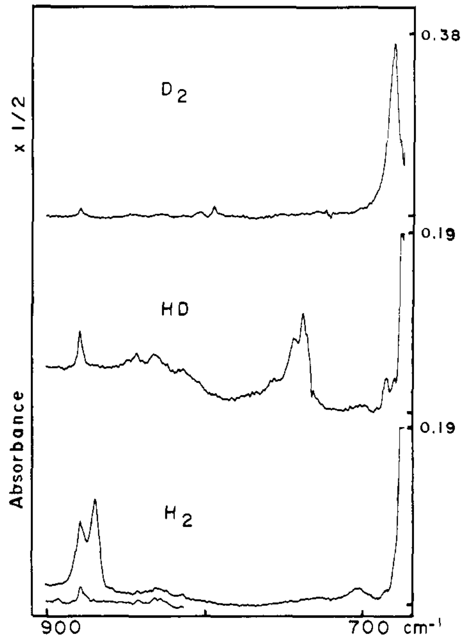

Figure 4. Spectra of $Cr(CO)_5(H_2)$ in the region of the $Cr–H_2$ stretching vibration. For all three spectra, the starting complex was $Cr(CO)_5NH_3$. Deposits were made for 4 h with argon doped with 20 mol % of hydrogen. In order to facilitate the comparisons, the intensity scales were adjusted so that the area under the totally symmetric breathing mode at 2095–2097 cm^{-1} was the same in all the matrices. The feature for the D_2 isotopomer is so much more intense than the corresponding features for the HD and H_2 isotopomers that it is plotted on a scale that is half as sensitive as the scale used for the other two. This increased intensity is due to Fermi resonance with the M–C–O deformation mode of A_1 symmetry and due to the reduced splitting of the mode itself. (The inset in the diprotium spectrum shows the size of the absorption due to a combination band of $Cr(CO)_6$ prior to irradiation.)

Table III. Overtones and Combination Bands of $Cr(CO)_5(H_2)$ Formed from $Cr(CO)_5NH_3$ between 4100 and 2400 cm^{-1} [a]

$Cr(CO)_5(H_2)$	$Cr(CO)_5NH_3$	$Cr(CO)_5(H_2)$	$Cr(CO)_5NH_3$
4064.2	4009.1	2690[b]	
4057.8	4009.1	(2673) [2670]	
3992.1	3992.9	2543 (2541) [2535]	2519.4
3974.1	3911.5, 3907.0	2460 (2456) [2450]	2425.9
3241	3294	2435	2426
2765		2428	2418
2690	2645		2408

[a] All peak positions are in cm^{-1}, obtained from FTIR spectra of nominal resolution of 1 cm^{-1}. The accuracy of the positions in many cases will be influenced by the presence of nearby absorptions. In situations in which there is a strong mass dependence, the position for the HD isotopomer will be in parentheses, that for the D_2 isotopomer will be in brackets. [b] Braod feature seen only in NH_3-containing matrices after extensive irradiation.

in the following paragraphs *does not* require the presence of ammonia.

The Hydrogen-Containing Vibrational Coordinates. Most of the hydrogen-containing vibrational features have been observed in the region from 600 to 3100 cm^{-1}. With the aid of FTIR, the hitherto unobserved H–H stretch has been observed of $Cr(CO)_5(H_2)$, which has been generated from $Cr(CO)_6$ in Ar/H_2 matrices. Figures 2 and 4 show the spectrum in the regions of the H–H stretch and the $M–H_2$ stretch for the various isotopomers.

Diprotium. In liquid Xe, the H–H stretch of $Cr(CO)_5(H_2)$ appears at 3030 cm^{-1} with a width at half-height of 38 cm^{-1}.[5] The width of the correlated band for the H–D isotopomer is more narrow and, for D_2, the band is most narrow.[13] In matrices, the H–H stretching region is similar for $Cr(CO)_5(H_2)$ formed from *both* $Cr(CO)_6$ and $Cr(CO)_5NH_3$, but is radically different from what is observed in liquid Xe. Three bands are present at 3087, 3027, and 2997 cm^{-1}. (See Table II.) The intensity of the band at 3027 cm^{-1} does not correlate with the other two bands. This lack of correlation is particularly apparent in the presence of 3% NH_3. The bands at 3087 and 2997 cm^{-1} are easily observed whereas the band at 3027 cm^{-1} is barely present. Although the intensities of the bands at 3087 and 2997 cm^{-1} are more strongly correlated, they occasionally do not show the same rate of growth in all experiments. The same three bands are observed in krypton matrices but the central peak is more prominent. (See Figure 3.) In Xe matrices, scattering makes observations at 3000 cm^{-1} more difficult. In order to obtain adequate signal-to-noise, difference spectra from three experiments were added together. It appears that there is a single broad absorption at 3025 cm^{-1} with very poor signal-to-noise.

A broad band at 1380 cm^{-1} is observed that corresponds to one observed by Turner.[13] The band is so weak and broad as to make the assignment very tentative. It corresponds to the asymmetric $M–H_2$ stretch that was first reported by Kubas for $(H_2)W(PR_3)_2(CO)_3$. A pair of bands at 878 and 869 cm^{-1} correspond to the symmetric $M–H_2$ stretch. These bands were not reported by Turner.[5,13] The presence of a nearby combination band of $Cr(CO)_6$ may have obscured them in Turner's experiments. Lastly, a broad band is observed at 2690 cm^{-1}. It is nearly twice as intense as the combination bands found in the region. (See Table III.) Its origin is unclear. It is not present in spectra of $Cr(CO)_5(H_2)$ formed from $Cr(CO)_6$. No similarly intense band that correlates with this band was observed in the spectrum of the heavier isotopomers. It is also noteworthy that the band becomes significantly broadened with prolonged irradiation.

Interestingly, CH_4 is a frequent impurity[15] and the C–H stretching modes have interfered with the observation of the H–H stretching mode. The methane is formed during the deposition of the matrix; when D_2 is present, CD_4 is observed. The methane is very dilute and is not affected by irradiation as judged by the deformation mode; thus the offending peaks can be removed by a simple subtraction of spectra taken before and after irradiation.

Deuterium Hydride. A broad absorption is observed in the region of the H–D stretch. The presence of ammonia causes

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(15) $M(CO)_6$ that is adsorbed on porous Vycor and other silica surfaces catalyzes the formation of methane from hydrogen and carbon monoxide. Consistent with the endogeneous source, the methane that is produced is fully deuterated when matrices are formed from D_2/Ar. The catalyst is presumed to be due to decomposition of $Cr(CO)_6$ on the glass transit tube through which the matrix gases and $M(CO)_6$ travel prior to deposition. Brenner, A.; Hucul, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 2484–2487.

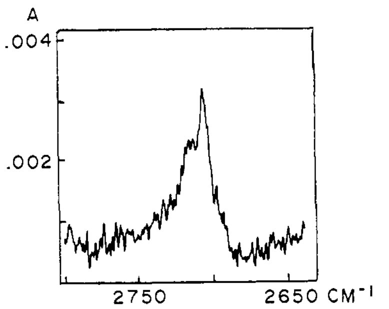

Figure 5. The H–H stretching region of $W(CO)_5(H_2)$. The spectrum was made after a 4.5-h deposit of 19% hydrogen in argon and 2.5 h of irradiation with a 500-W projector lamp. The spectrum is the average of 200 scans. The totally symmetric A_1 vibration of the carbonyl ligands at 2102 cm^{-1} had achieved 0.013 optical density units.

additional intensity to be present on the low-frequency side of the peak. Sometimes the band shows structure which suggests that it could be resolved into two or perhaps three components. The width of the band at half-height is 22 cm^{-1}, somewhat more narrow than what is observed in liquid Xe.[13] Never is the spread of frequencies anywhere as great as is observed for the bands assigned to the H–H stretch. The band that corresponds to the symmetric M–HD stretch appears at 741 cm^{-1} and is also split but not to the same extent as for diprotium.

Dideuterium. The presence of ammonia in the matrix perturbs the D–D stretching vibration, adding intensity on the low-frequency side of the peak just as was found to be the case for the H–D stretch. The band exhibits contours that make it appear to be an envelope of several partly resolved bands. In this, it mimics the behavior of the H–D stretch. The width of the band is 19 cm^{-1}, nearly the same width as observed in liquid Xe.[13] The band at 680 cm^{-1}, which has been observed in previous studies, is unsymmetrical.[1,13] This band is assigned to the M–D_2 stretch and correlates with the pairs of resolved absorptions in the spectrum of $Cr(CO)_5(H_2)$ and $Cr(CO)_5(HD)$. The shape of the M–D_2 suggests an unresolved splitting similar to, but smaller than, the lighter isotopomers.

$W(CO)_5(H_2)$. The behavior of $W(CO)_5NH_3$ in hydrogen-containing matrices mimics that of $Cr(CO)_5NH_3$ in many respects. Irradiation with visible light in the presence of hydrogen gives $W(CO)_5(H_2)$, the carbonyl bands of which are split in a similar fashion to those of II. Two overlapping absorptions are observed in the H–H stretching region at 2708 and 2719 cm^{-1}; overall the two have a width of 20 cm^{-1} at half-height. (See Figure 5.) These correspond to a band observed in liquid xenon at 2711 cm^{-1}.[13,16] Unfortunately, the H–D and D–D appear in regions of the spectrum that are very difficult to measure. The H–D stretch is in the vicinity of atmospheric absorptions due to CO_2. Tentatively, we assign a band at 2370 cm^{-1} to that vibration. The D–D stretch is expected in the region of the carbonyl vibrations. The mode cannot be strongly coupled to the carbonyl modes because carbonyl modes appear at nearly identical positions for H_2 and D_2 adducts. One of the peaks in the complex at 1970 cm^{-1} is shifted to lower frequency by about 1 wavenumber.

Some of the other hydrogen vibrational coordinates have also been observed. The vibration corresponding to the H_2–W stretch is observed at 899 cm^{-1}. The band was observed at 919 cm^{-1} in liquid Xe.[13] The corresponding feature appears in the spectrum of $W(CO)_5(HD)$ at 751 cm^{-1}. Signal-to-noise does to permit a determination of a splitting. The W–D_2 stretch was not observed. It is conceivable that it is obscured by an absorption due to CO_2 at 667 cm^{-1}.

Discussion

The H–H stretching mode of coordinated dihydrogen has been observed for several other complexes.[5,13,17-19] The hydrogen-mass-dependent width of the mode was initially ascribed to rapid rotation of the hydrogen molecule about the principal axis of $Cr(CO)_5$.[13] More recently, exchange phenomena were considered the more likely cause.[20] The multiple absorptions that have been observed in this study have only one precedent. The H–H stretching region of $Co(CO)_2NO(H_2)$ exhibits two absorptions. They were attributed to Fermi resonance between the H–H stretch and overtones or combination bands.[18] Like $Cr(CO)_5(H_2)$, the splitting is only observed for the diprotium isotopomer. Other hydrogen-containing vibrational coordinates also show splittings. The spectrum of $(H_2)W(PR_3)_2(CO)_3$ exhibits a splitting of 45 cm^{-1} in the torsional mode at 350 cm^{-1}.[21] The splitting has been attributed to nearly free rotation of the hydrogen about the molecular 2-fold axis. From the splitting, a barrier to rotation of 760 cm^{-1} was calculated. The spectrum of PdH_2 also exhibits a splitting in an absorption assigned to the M–H_2 stretching vibration.[22] This splitting was also attributed to hindered rotation of the hydrogen.

The barrier to H_2 rotation of $(H_2)Cr(CO)_5$ is undoubtedly smaller than what is exhibited by $(H_2)W(PR_3)_2(CO)_3$. We offer two reasons. First, the hydrogen interacts less strongly with chromium than with tungsten as judged by the H–H and the M–(H_2) stretching frequency and, second, the absence of bulky phosphines in the equatorial positions should allow more facile rotation. Nevertheless, it is unlikely that there is free rotation at 10 K. An analysis of the spectra also argues against there being free rotation. Consider the pair of bands at 2996 and 3089 cm^{-1}. A referee has reminded us that they are separated by nearly 2B if one assumes an H–H distance is greater than 82 pm. Suppose that they arose from vibrational transitions that were coupled to different rotational levels. It is difficult to rationalize why the same structure is not observed in liquid Xe at much higher temperature, or in solid Xe.

In the context of discussions of the rotation of hydrogen, it is appropriate to consider whether differing nuclear spin states of hydrogen are causing the splittings of the H–H stretching region. We have observed no differences between the spectrum produced by an ortho–para mixture characteristic of room temperature and the spectrum produced by a mixture that was enriched in para hydrogen. Since differing mixtures of ortho and para hydrogen do not result in detectable changes in the H–H stretching region, then one of the two conclusions can be made. Either the spectrum is not perturbed by the nuclear spin state of the hydrogen or the spectrum is due to only the para form. The nuclear spin state of the hydrogen which is coordinated to chromium is not apparent from our data. If, during irradiation, the chromium is converted to a triplet, then it may catalyze the conversion of ortho to para hydrogen of those molecules in the immediate vicinity of the chromium. If this occurs, then it will make no difference what the ortho–para composition is in the deposit mixture; the composition of spin states in the matrix will be that characteristic of 10 K. Even if odd *J* states existed for freely rotating, coordinated para hydrogen, the intensity of the band at 3087 cm^{-1} relative to the band at 2997 cm^{-1} seems too large to assume that the two bands are due to freely rotating para hydrogen. Rather we believe that these feature are not affected by the nuclear spin states of hydrogen.

If one allows for the possibility that the rotation is hindered, then it is still difficult to rationalize the data. A barrier may be

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intramolecular in origin or it may arise from packing effects or interactions between ammonia and the hydrogen. For moderately low barriers the hydrogen can rotate at low temperature by tunneling through the barrier just as was observed for $(H_2)W(PR_3)_2(CO)_3$. The vibrational feature that will be most affected by rotational tunneling is the torsional mode that corresponds to the damped rotation of the hydrogen. The mode should be split to the degree that the barrier to rotation is low.[23] The effect of rotational tunneling on the other modes should be less pronounced just as the inversion splitting of ammonia is observed only in those modes that translate the nitrogen atom along the 3-fold axis; that motion is most related to inversion.[23,24] In particular, the motions of an H–H stretch or an $M-H_2$ stretch do not contain any components of a rotation of the hydrogen about the 4-fold axis of chromium. The motions are of different symmetries and cannot mix. We cite the analogous behavior of OH rotation in methanol. Only the torsional mode exhibits splitting due to the hindered rotation in the ground-state molecule.[25,26] Thus, no splitting of the H–H stretching vibration is expected due to hindered rotation; the symmetry is wrong. Additionally, the degree of splitting does not vary as the composition of the matrix is varied. Such variation should affect the intermolecular contribution to the barrier and result in different spacings if the splitting were due to rotational tunneling. It should also be noted that mixing of the stretching coordinate and the librational mode will not become allowed if the hydrogen axis of rotation is moved off the 4-fold axis of the $Cr(CO)_5$ moiety.

It is unlikely that overtones or combination bands occur in the region of the H–H stretch so that Fermi resonance enhancement would be observed. A number of combination bands and overtones have been observed for II. (See Table III.) In every instance they result from the $Cr(CO)_5$ part of the molecule and correlate strongly with bands that are observed for $Cr(CO)_5NH_3$. Detailed studies of $Cr(CO)_6$ show no features in the region of 3000 cm^{-1}.[27] The absence of strong coupling between the $Cr(CO)_5$ part of the molecule and the H_2 makes it unlikely that combination bands arising from carbonyl and hydrogen-containing modes will be important. The positions of these combinations can be estimated from what is known of the spectrum of $Cr(CO)_5(H_2)$ and $(H_2)W(PR_3)_2(CO)_3$. No combinations of two fundamentals will occur between 3100 and 3000 cm^{-1}. The combinations that bracket this region include a combination between the totally symmetric breathing mode of the carbonyls and the $Cr-H_2$ stretch at or below 2965 cm^{-1} and the combination between either the E symmetry carbonyl band and the assymmetric $M-H_2$ stretch at or below 3350 cm^{-1}.

The interactions with ammonia that are responsible for the splitting of the carbonyl modes are not responsible for the splitting in the M–H stretching region. The same splittings are observed for $Cr(CO)_5(H_2)$ whether it is formed from $Cr(CO)_6$ or from $Cr(CO)_5NH_3$. Moreover, the intensities of the various H–H stretching vibrations do not correlate with the features assigned to a particular trapping site of II. It does not appear that concentration effects are causing the splittings. The splitting in argon has been observed with hydrogen concentrations ranging from 7 to 22 mol %. Although the doping level of I is not known, it is unlikely that near-neighbor interactions occur to a significant extent because the behavior of the carbonyl modes does not vary as a function of the sublimation temperature.

In considering the possibility of different intermolecular interactions we next consider a mechanism for splitting based on analogies of exchange processes observed principally by NMR. Again, the theory cannot explain the data. If one assigns two of the H–H stretching vibrations to different environments for $Cr(CO)_5(H_2)$ while assigning the central peak to a weighted average, then nearly all the behavior of diprotium can be explained, but one must also observe the same splitting in the spectrum of dideuterium. If tunneling plays a role in the site exchange, then the dideuterium spectrum should more likely give evidence of *slow* exchange and thus show the several bands. Turner et al. had wondered whether the width of the band at 3030 cm^{-1} in liquid xenon might be due to exchange effects, but they lacked the low-temperature data[20]. These data would also suggest that exchange is not responsible for the width as well.

The $M-H_2$ stretching vibration is also split in argon matrices. In solid xenon, there is only a single broad absorption. The causes for this behavior may be similar to what causes the complexity in the H–H stretching region. $Cr(CO)_5(H_2)$ formed from $Cr(CO)_6$ also exhibits splitting; so it is clear the splitting is not due to the presence of a nearby ammonia molecule. A splitting was observed in the spectrum of PdH_2.[22] This splitting was attributed to hindered rotation of the hydrogen, and Mathieu's functions were used to treat the problem. This explanation seems unlikely for reasons that were stated above. The reasons for splitting of the $M-H_2$ vibration and the H–H stretching vibration are undoubtedly linked.

Two phenomena require an explanation: the width and the splitting of the H–H stretching vibration. The width of the central absorption at 3027 cm^{-1} is similar to what is observed in liquid Xe at higher temperatures. The width is independent of temperature and the composition of the matrix. The fact that the isotopomer with least mass is most affected suggests that hindered rotational motion is involved in the complexity. This strange behavior of diprotium may reflect the large amplitude of the torsional vibration. The amplitude for a harmonic vibration varies as the inverse fourth root of the reduced mass.[28] Thus, the torsional motion for diprotium is 20% greater than for dideuterium. For a softer potential such as a cos $(n\Theta)$ potential, the amplitude differences could be even more extreme. By this way of thinking diprotium would sample a more varied environment than either HD or D_2. During the excursion, the stretching frequency would still be sufficiently rapid that all environments would not be averaged.

It appears that the presence of the two bands at 3087 and 2997 cm^{-1} is due to the hydrogen-containing host lattice, but the effect is not the usual site effect, because neither HD nor D_2 are similarly affected. If the only difference between the diprotium and dideuterium spectra was due to the effect of different reduced masses on typical vibrational transitions, then analogous features would appear between 2220 and 2287 cm^{-1}. The matrix property that seems to correlate best with the behavior of the bands at 3087 and 2997 cm^{-1} is size. In particular, the bands at 2997 and 3087 cm^{-1} are most prominent when the size of the matrix host molecule is smallest. In argon matrices doped with additional ammonia, the bands at 3087 and 2997 cm^{-1} are much more prominent relative to the band at 3027 cm^{-1} than they are in pure argon. Since the van der Waals radius of ammonia is smaller than that of argon, one can presume that $Cr(CO)_5(H_2)$ is more crowded when ammonia is present. The crowding should be less pronounced in Kr, and one observes the band in the center at 3025 cm^{-1} to be most prominent. (See Figure 3.) To repeat, the complexity cannot be attributed to site effects alone or the H–D and D–D stretch would be similarly affected; the hindered rotation of H_2 on chromium must also play a role. The crowding of the matrix atoms around II may force the rotation of the hydrogen molecule off the 4-fold axis of the $Cr(CO)_5$ moiety. We have argued that coupling between the torsional mode and the H–H stretch still is forbidden. We know of no theory that explains the splitting, yet in the preceding paragraphs we have shown that a variety of explanations fail to account for the splittings. Still, it seems clear that cause must be related to the hinder rotation of the hydrogen. The behavior of $W(CO)_5(H_2)$ provides an inter-

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esting contrast. Both the width of the vibration and the absence of splittings make the H–H stretch similar to the D–D stretch of II. The solution to this problem must await further theoretical developments.

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Registry No. $Cr(CO)_5NH_3$, 15228-27-0; Ar, 7440-37-1; Xe, 7440-63-3; Kr, 7439-90-9; $Cr(CO)_5(H_2)$, 102286-49-7; D_2, 7782-39-0; H_2, 1333-74-0; $Cr(CO)_5$, 26319-33-5; $W(CO)_5NH_3$, 15133-64-9; $W(CO)_5(H_2)$, 102286-51-1; $Cr(CO)_5(HD)$, 102286-52-2; $Cr(CO)_5(D_2)$, 102286-55-5; $W(CO)_5(HD)$, 119907-64-1; $W(CO)_5(D_2)$, 117340-06-4.

Supplementary Material Available: A detailed description of the influence of ammonia on the spectrum of II, including two tables and two figures (13 pages). Ordering information is given on any current masthead page.

Electronic Structure Factors of Si–H Bond Activation by Transition Metals. The Valence Photoelectron Spectrum of $(\eta^5\text{-}C_5H_5)Mn(CO)_2HSiCl_3$

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Abstract: The valence photoelectron spectra of $HSiCl_3$ and $CpMn(CO)_2HSiCl_3$ ($Cp = \eta^5\text{-}C_5H_5$) have been obtained to provide a measure of the electronic structure factors that contribute to the interaction of the Si–H bond with a transition-metal center. The lowest valence ionizations of other $CpMn(CO)_2$(ligand) complexes are metal-based and reflect the formal d^6 electron count at the metal. The lowest valence ionizations in the He I photoelectron spectrum of $CpMn(CO)_2HSiCl_3$ are more stable and split over a wider energy range than has been observed previously. The chlorine lone pair based ionizations of $HSiCl_3$ coordinated to the metal have shifted about 1 eV to lower ionization energy from those of the free $HSiCl_3$ molecule. Both the stabilization of the metal-based ionizations and the destabilization of the ligand-based ionizations show that electron charge shift from the metal to the ligand more than compensates for the initial σ donation from the Si–H bond to the metal in $CpMn(CO)_2HSiCl_3$, as expected if the bonding has proceeded significantly toward oxidative addition. The relative intensity of the higher ionization energy component in the metal ionization region decreases with He II excitation, showing that this band is actually associated more with ligand character. This He I/He II relative intensity behavior corresponds to a formal d^4 electron count for the metal, consistent with the Mn(III) oxidation state. Fenske-Hall calculations indicate that the metal d hybrid orbitals available for the Mn–Si and Mn–H bonds form an acute angle between 50° and 70°, and these directed hybrids are responsible for the close proximity of the silicon and hydrogen atoms in the complex. These results are related to the other physical and chemical properties of this complex and are contrasted with the results of our similar photoelectron studies on the interaction of a carbon–hydrogen bond with the metal center in $(\eta^3\text{-}C_6H_9)Mn(CO)_3$, where the interaction primarily involves donation of C–H σ bonding orbital electron density into the empty metal orbitals in the formation of a 3-center 2-electron bond.

Knowledge of the factors controlling bond activation processes by transition metals is fundamental to understanding many important chemical reactions. The carbon–hydrogen bond is clearly one of the most desirable bonds to activate, and the interaction of the C–H bond with transition-metal centers has received much attention.[1-7] The general electronic factors of the bond activation process have been conveniently discussed in terms of a simple model in which there are two limiting descriptions of the electron distribution in the interaction.[8] In the early stages of the process σ activation is taking place, in which electron density from the C–H σ bond is donating into available empty metal levels to form a 3-center 2-electron bond. This interaction may be accompanied by competing filled–filled orbital interactions (i.e. steric repulsions) that will also play an important role in determining whether activation of the C–H bond will actually take place. For the C–H bond to be completely broken, the second stage of activation must take place in which electron density from filled metal levels donates into the empty C–H σ^* orbital, thereby completing the oxidative addition to formation of the alkyl metal hydride.

The electronic structure factors of C–H activation have been the subject of numerous theoretical investigations.[9-12] Photoelectron spectroscopy is able to provide direct experimental information on the strengths of individual bonding interactions with the metal center and the electron richness and charge potential throughout the complex.[13-15] An example is provided by the

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